CONTENTS

Page.

HEISE, GEORGE W. Notes on the water supply of the city of Manila 1

BRILL, HARVEY C., and AGCAOILI, FRANCISCO. Philippine beeswax 15

KING, ALBERT E. W. The pozzuolanic properties of Meycauayan volcanic tuff 19

HEISE, GEORGE W., and AGUILAR, R. H. The oxygen-consuming power of natural waters 37

The "Philippine Journal of Science" is issued as follows:	U. S. currency.
Section A. Chemical and Geological Sciences and the Industries..	$2.00
Section B. Tropical Medicine	3.00
Section C. Botany	2.00
Section D. General Biology, Ethnology, and Anthropology (Section D began with Volume V)	2.00
Entire Journal, Volume II, III, IV, or V	5.00
Entire Journal, beginning with Volume VI	7.00
Single numbers (except of Volume I)	.50

Each section is separately paged and indexed.
Authors receive 100 copies of their papers free.

Volume I, 1906 (not divided into sections) and supplement, sold only with a complete file of section A, B, or C..........	10.00
Supplement to Volume I (botany)	3.50
Volume I (without supplement), sold only with a complete file of section A, B, or C..........	6.50
Single numbers of Volume I	.75

Publications sent in exchange for the Philippine Journal of Science should be addressed: Library, Bureau of Science, Manila, P. I.

Subscriptions may be sent to the BUSINESS MANAGER, Philippine Journal of Science, Bureau of Science, Manila, P. I., or to any of the agents listed below:

AGENTS

The Macmillan Company, 64–66 Fifth Avenue, New York City, U. S. A.
Wm. Wesley & Son, 28 Essex Street, Strand, London, W. C., England.
Martinus Nijhoff, Lange Voorhout 9, The Hague, Holland.
Mayer & Müller, Prinz Louis Ferdinandstrasse 2, Berlin, N. W., Germany.
Kelly & Walsh, Limited, 32 Raffles Place, Singapore, Straits Settlements.
A. M. & J. Ferguson, 19 Baillie Street, Colombo, Ceylon.
Thacker, Spink & Co., P. O. Box 54, Calcutta, India.

Entered at the post office at Manila, P. I., as second-class matter.

VOL. XI, SEC. A, NO. 2 MARCH, 1916

THE PHILIPPINE JOURNAL OF SCIENCE

ALVIN J. COX, M. A., PH. D.
GENERAL EDITOR

SECTION A

CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF

W. E. PRATT, A. M.; H. C. BRILL, PH. D.; J. R. WRIGHT, PH. D.
G. W. HEISE, M. S.; J. C. WITT, PH. D.; T. DAR JUAN, A. B.
R. C. McGREGOR, A. B.; H. E. KUPFER, A. B.

BUREAU OF SCIENCE
MANILA

MANILA
BUREAU OF PRINTING
1916

PUBLICATIONS FOR SALE BY THE BUREAU OF SCIENCE, MANILA, PHILIPPINE ISLANDS

ETHNOLOGY

A VOCABULARY OF THE IGOROT LANGUAGE AS SPOKEN BY THE BONTOC IGOROTS

By Walter Clayton Clapp

Order No. 408. Paper, 89 pages, $0.75, postpaid.

The vocabulary is given in Igorot-English and English-Igorot.

THE NABALOI DIALECT

By Otto Scheerer

and

THE BATAKS OF PALAWAN

By Edward Y. Miller

Order No. 403. Paper, $0.25; half morocco, $0.75; postpaid.

The Nabaloi Dialect (65 pages, 29 plates) and the Bataks of Palawan (7 pages, 6 plates) are bound under one cover.

THE BATAN DIALECT AS A MEMBER OF THE PHILIPPINE GROUP OF LANGUAGES

By Otto Scheerer

and

"F" AND "V" IN PHILIPPINE LANGUAGES

By Carlos Everett Conant

Order No. 407.

These two papers are issued under one cover, 141 pages, paper, $0.80, postpaid.

THE SUBANUNS OF SINDANGAN BAY

By Emerson B. Christie

Order No. 410. Paper, 121 pages, 1 map, 29 plates, $1.25, postpaid.

Sindangan Bay is situated on the northern coast of Zamboanga Peninsula. The Subanuns of this region were studied by Mr. Christie during two periods of five and six weeks, respectively.

The 29 plates illustrate the Subanuns at work and at play; their industries, houses, altars, and implements; and the people themselves.

THE HISTORY OF SULU

By Najeeb M. Saleeby

Order No. 406. Paper, 275 pages, 4 maps, 2 diagrams, $0.75, postpaid.

In the preparation of his manuscript for The History of Sulu, Doctor Saleeby spent much time and effort in gaining access to documents in the possession of the Sultan of Sulu. This book is a history of the Moros in the Philippines from the earliest times to the American occupation.

ETHNOLOGY—Continued

STUDIES IN MORO HISTORY, LAW, AND RELIGION

By Najeeb M. Saleeby

Order No. 405. Paper, 107 pages, 16 plates, 5 diagrams, $0.25; half morocco, $0.75; postpaid.

This volume deals with the earliest written records of the Moros in Mindanao. The names of the rulers of Magindanao are recorded in five folding diagrams.

NEGRITOS OF ZAMBALES

By William Allan Reed

Order No. 402. Paper, 83 pages, 62 plates, $0.25; half morocco, $0.75; postpaid.

Plates from photographs, many of which were taken for this publication, show ornaments, houses, men making fire with bamboo, bows and arrows, dances, and various types of the people themselves.

INDUSTRIES

PHILIPPINE HATS

By C. B. Robinson

Order No. 415. Paper, 66 pages, 8 plates, $0.50 postpaid.

This paper is a concise record of the history and present condition of hat making in the Philippine Islands.

THE SUGAR INDUSTRY IN THE ISLAND OF NEGROS

By Herbert S. Walker

Order No. 412. Paper, 145 pages, 10 plates, 1 map, $1.25, postpaid.

Considered from the viewpoint of practical utility, Mr. Walker's Sugar Industry in the Island of Negros is one of the most important papers published by the Bureau of Science. This volume is a real contribution to the subject; it is not a mere compilation, for the author was in the field and understands the conditions of which he writes.

A MANUAL OF PHILIPPINE SILK CULTURE

By Charles S. Banks

Order No. 413. Paper, 53 pages, 20 plates, $0.75, postpaid.

In A Manual of Philippine Silk Culture are presented the results of several years' actual work with silk-producing larvæ together with a description of the new Philippine race.

THE PHILIPPINE
JOURNAL OF SCIENCE
A. CHEMICAL AND GEOLOGICAL SCIENCES
AND THE INDUSTRIES

VOL. XI MARCH, 1916 No. 2

THE CHEMISTRY OF THE VITAMINES[1]

By ROBERT R. WILLIAMS
(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Since the appearance of the last article in which I collaborated with Doctor Vedder,[2] I have made more than forty attempts to obtain pure vitamine from large quantities of rice polishings. While other methods were tried, the prime endeavor was to perfect the method described by Funk,[3] as it appeared to be preferable to that of Edie et al.[4] or Suzuki[5] and his coworkers, with whose methods I have experimented. The modification of Wellman, Eustin, and Scott[6] was also tested. It failed to facilitate the final purification of the vitamine and apparently resulted in greater loss of curative power in the vitamine fraction. On the other hand, it possesses the great advantage of effecting an enormous saving in the quantities of phosphotungstic acid and barium hydroxide used.

In addition to these methods, many other precipitants have been tried, such as mercuric acetate and zinc and cuprous salts, but of these none produced promising results and may be dismissed. Other attempts were directed to finding a better method of decomposing the phosphotungstates produced by Funk's method. For this purpose amyl alcohol was used as suggested by Jacobs.[7] This, however, afforded no particular advantage, as the vitamine apparently distributed itself more or less equally between the amyl alcohol and water layers. It was also discovered that the phosphotungstate of the vitamine dissolved fairly readily in an excess of phosphotungstic acid, thus enabling it to be separated from the bulk of the precipitated phosphotungstates. But since barium hydroxide was the only reagent found which could be used effectively for decomposing the separated phosphotungstates, this method was also abandoned.

---

[1] Received for publication April 26, 1915.

[2] *This Journal, Sec. B* (1913), 8, 175.

[3] *Journ. Physiol.* (1911), 43, 395; (1912), 45, 75; *Ergeb. d. Physiol.* (1913), 13, 125.

[4] *Bio-chem. Journ.* (1912), 6, 234.

[5] *Bio-chem. Zeitschr.* (1912), 43, 89.

[6] *Am. Journ. Prev. Med.* (1914), 1, 295.

When it was desired to isolate considerable quantities of vitamine in a fairly pure or at least highly concentrated condition, it was necessary to fall back on the method of Funk in practically its original form as nearly as I now understand it. This was the method used for the treatment of the human cases recently reported by Doctor Saleeby and me.[8]

Every resource has been exhausted to avoid mixed deposits from the final liquor and to increase the yield of needles melting at 233°, but without avail. Every step in the process has been modified in turn, but without materially improving the final result. Among such modifications may be mentioned the following:

1. Varying degrees of expression of the original polishings.
2. The use of neutral alcohol for extraction and subsequent hydrolysis of the aqueous extract with dilute sulphuric acid.
3. The use of a glass still and high vacuum for concentrating the extract.
4. More or less prolonged maceration of the phosphotungstates with barium hydroxide.
5. Removal of ammonia from the resulting solution with a stream of air.
6. Varying the strength of reagents and solvents at many points in the process.

I was, therefore, at a loss for an adequate explanation of the discrepancies between my results and those of Funk. Recent work[9] now shows that Funk was in error in reporting the isolation of the curative substance as a pure chemical individual and that the substance melting at 233° consisted almost entirely of nicotinic acid. A number of other differences exist between Funk's results and my own, which are not as yet wholly accounted for. I have noted that the quality of the rice polishings appears to affect the yield of curative substances considerably and have selected the raw material accordingly. Perhaps more suggestive is the idea which has but recently occurred to me that rice polishings, like yeast,[10] may undergo an autolysis which splits the mother substances of the vitamines in a different way than does acid hydrolysis. Funk obtained his entire supply of rice polishings from the Orient,[11] and the bran was well aged before being submitted to chemical manipulation. Here comparatively fresh material has been used uniformly on account of the difficulty of protecting it during storage from the attacks of insects which multiply in it with tremendous rapidity. The presence of large quantities of enzymes in rice polishings is readily demonstrable, as there is rapid production of carbon dioxide from its suspensions in water in the presence of sufficient formaldehyde or phenol to prevent bacterial growth.

---

[7] *Journ. Biol. Chem.* (1912), **12**, 429.

[8] *This Journal, Sec. B* (1915), **10**, 99.

[9] Drummond and Funk, *Biochem. Journ.* (1914), **8**, 598.

In as much as Funk's descriptions of his chemical methods have been so brief and incomplete as to puzzle me greatly, the method as used by myself is recorded in detail, with notes on the apparent discrepancies in results.

Hope of isolating large quantities of an individual vitamine from rice polishings having been abandoned, it was decided to attempt the synthesis of curative substances, which might throw light on the nature of the vitamines. As a discontinuance of the work for the present is now necessary, the very incomplete results are reported in the experimental part.

In choosing the direction for a beginning in this work, the facts adduced by Funk and others pointed to the pyridine ring as the most promising nucleus. The most important facts in favor of this choice are the occurrence of nicotinic acid with the vitamine in several natural substances and the resistance of the vitamine to the Kjeldahl method of digestion for the determination of nitrogen. That this property of the vitamine is shared to the greatest degree by bodies containing the pyridine ring has been shown by the as yet incompleted work of Doctor Brill and Mr. Agcaoili of the Bureau of Science who have kindly communicated their results to me. This resistance is well exemplified by the method of Weidel and Murmann [12] for preparing pyridine sulphonic acids.

---

[10] Cooper, *Biochem. Journ.* (1914), 8, 250; Abstract in *Zentralbl. Biochem. u. Biophysik.* (1914), 17, 481.

[11] *Journ. Physiol.* (1911-1912), 43, 400.

[12] *Monatsh. f. Chem.* (1895), 16, 749.

SCIENTIFIC LIBRARY
INSTITUTE OF SCIENCE
(Formerly Bureau of Science)
Manila

The earlier surmise of Funk that the vitamines are purine or pyrimidine derivatives, on the other hand, does not appear to agree with the known facts above cited. It is supported by the semicurative properties of allantoin and other purine and pyrimidine bodies, which is, however, largely offset by the similar though less-marked property of nicotinic acid. No doubt the conception of the vitamines as necessary foodstuffs for the elaboration of certain tissue constituents had weight with Funk in this surmise. Experience with human beriberi, however, throws much doubt on the truth of this conception, the evidence against which is presented elsewhere.[18]

EXPERIMENTAL PART

METHOD OF SEPARATION OF THE VITAMINE OF RICE POLISHINGS

Twenty-five kilograms of selected, finely ground, light-colored rice polishings are allowed to macerate with occasional stirring for from twelve to twenty-four hours in a mixture of 75 liters of 95 per cent alcohol and 5 liters of concentrated hydrochloric acid. The mass is then pressed out at a pressure of about 1,000 pounds to the square inch. The collected liquid amounts to from 60 to 65 liters. It is evaporated in a copper still at a pressure of from 10 to 12 centimeters of mercury to a volume of about 3 liters. The concentration requires about seven hours. The temperature should not rise above 50°. The concentrated extract separates into layers of fat and aqueous liquid. The aqueous extract is separated from the fat while still warm and is filtered from a copious black sediment, which after being washed is discarded with the fat. The filtered extract and washings are further concentrated in glass under a good vacuum to 2 liters.

Phosphotungstic acid is added gradually till permanent precipitation is complete. An excess must be avoided. Some samples of phosphotungstic acid were encountered which produced temporary precipitates which later redissolved when concentrated solutions were added to an extract already completely precipitated. Therefore care should be taken that the further precipitation is permanent. After standing overnight, the precipitated phosphotungstates are collected and thoroughly washed with 5 per cent sulphuric acid till the washings show only traces of chlorides. When thoroughly air-dried the phosphotungstates so produced weigh from 2,200 to 2,500 grams, compared with about 450 grams obtained by Funk[14] from the same quantity of polishings. This large yield is somewhat, but not greatly, reduced if the original extract is made with neutral alcohol and the concentrated extract hydrolyzed by boiling with 10 per cent sulphuric acid under a reflux condenser for five hours. However, the maceration in acid alcohol produces an extract which cures neuritic fowls in doses corresponding to 50 grams, whereas extracts made by the latter method must be given in doses corresponding to 100 grams to produce the same result.

---

[18] Williams and Johnston, *This Journal, Sec. B* (1915), 10, 337.

The mass of dry phosphotungstates is ground intimately with two and a half times its weight of barium hydroxide. During this process the mixture becomes pasty and develops an evanescent green. The odor evolved is somewhat distinctive and resembles that of methyl amine. The pasty mass is collected in a large bottle and is shaken with 3 liters of water for five hours and filtered. The residue is again shaken twice with water for an hour each time. The combined filtrates, from which in the meantime the excess of barium hydroxide has been completely removed with sulphuric acid without the least unnecessary delay, are now carefully tested for excess of sulphuric acid or barium. Any excess of either having been carefully removed, the solution is neutralized with nitric acid, using litmus paper as indicator, and is concentrated in vacuo to a volume of about 1 liter. At this point the toxic properties of the liquid are so great that it is impossible to demonstrate its curative power.

To the concentrated liquid a 10 per cent solution of silver nitrate is added till no further precipitation occurs. The bulky yellow precipitates of purine bases are separated by filtration, and the filtrate is reserved for further fractionation. The purine bases are discarded. I am yet uncertain whether or not Funk carried out this separation of the purine bases in the case of rice polishings, although he reports having done so with yeast. At all events the purine bases so separated, although considerable in amount, do not when freed from silver possess curative properties to a high degree. Moreover it would be quite hopeless under my conditions of work to try to insolate any substance in a pure state from the vitamine fraction if the purines were included with it.

A small aliquot part of the filtrate from the purine bases is titrated with a 5 per cent silver nitrate solution till a drop of the clear titration liquid placed on a test plate gives with a saturated solution of barium hydroxide a distinctly brown rather than white or pale yellow precipitate. To the main portion of the filtrate from the purine bases is added an amount of silver nitrate slightly less than that calculated from the above titration.

---

[14] *Journ. Physiol.* (1912), 43, 396.

A small aliquot part of the resulting liquid is now titrated with a saturated solution of barium hydroxide. A white precipitate forms, which at first redissolves on stirring. Later the precipitate becomes permanent and gradually darkens. As long as insufficient barium hydroxide is present the precipitate will settle on standing a few minutes, leaving the supernatant liquid bright and clear. Upon the addition of an excess of barium hydroxide the supernatant liquid becomes cloudy or muddy in proportion to the excess of barium hydroxide. Having thus determined the quantity of barium hydroxide necessary, the aliquot part is combined with the main portion and the calculated quantity of barium hydroxide solution is added. A slight deficiency is preferable to an excess.

The method suggested by Funk of testing with ammoniacal silver nitrate to determine the necessary quantity of barium hydroxide was of very little use to me, as this reagent at no stage produces more than a faint precipitate with the filtrate from the vitamine fraction.

When the precipitation with barium hydroxide is completed, the precipitate is allowed to settle and after decantation of the clear liquid is collected on a Büchner funnel and is thoroughly washed with water. The precipitate, which has by this time assumed a dark green, is suspended in 100 cubic centimeters of water, into which is led a stream of hydrogen sulphide. The suspension is shaken continuously during the passage of the hydrogen sulphide, which continues for from thirty to forty minutes. The solution is filtered, and the precipitate is repeatedly macerated and washed with small quantities of water containing hydrogen sulphide. The combined washings and filtrate from the silver sulphide are carefully treated with very dilute sulphuric acid until all traces of barium are just removed. After filtering from barium sulphate, the solution is evaporated at room temperature to a volume of 50 cubic centimeters. One hundred cubic centimeters of 70 per cent alcohol are added. A rather copious, brown, flocculent precipitate results, which is separated by filtration and washed with 70 per cent alcohol. This precipitate has rather slight curative powers, a dose equivalent to 15 or 20 kilograms of the original polishings being necessary to cure a fowl. It gives the uric acid reaction.[15] It is fairly freely soluble in water, but is very slightly soluble in alcohol. From it considerable nicotinic acid can be crystallized from hot water.

The alcoholic filtrate and washings, which are now curative for fowls in doses equivalent to 3 kilograms of the original polishings as compared with 100 grams in the case of the original extract,[16] are collected and evaporated in a dessicator over sulphuric acid at ordinary pressure. A vacuum dessicator produces too rapid an evaporation for the best results. This solution is now distinctly acid to litmus, but not to methyl orange. As evaporation proceeds, the acidity diminishes. Occasionally a faint alkalinity is developed, resulting in considerable loss of curative power on further standing. In the course of a week's standing in the dessicator, a few needle crystals, 2 to 3 millimeters in length, appear. These show a marked tendency to float on the surface of the mother liquor. At the same time a deposit collects in the bottom of the vessel, consisting of mixed forms of crystals and much amorphous matter. The floating crystals when removed and dried melt at 233° and produce cures in fowls in doses of from 10 to 20 milligrams. The yield, however, amounts to only from 30 to 40 milligrams. If the crystals are allowed to remain in the mother liquor, there is no further accumulation. The amorphous material, however, gradually increases in amount. If separated when the volume has diminished to 10 or 12 cubic centimeters, it shows curative power in fowls in doses of from 20 to 30 milligrams. The yield from 25 kilograms of polishings amounts to 0.2 to 0.25 gram. It is difficultly soluble in water and alcohol and when recrystallized from dilute alcohol is very little altered in appearance or character. This is the product which was used in treating the human cases recently reported.[17]

On further evaporation of the mother liquor from this product either with or without the addition of alcohol, a syrup results which eventually dries to a hard clear film, weighing from 0.2 to 0.3 gram. It possesses curative properties in mod-

---

[15] Folin and Macallum, jr., *Journ. Biol. Chem.* (1912), **11**, 265; (1912–13), **13**, 363.

[16] Funk's statement that the vitamine fraction retains nearly the whole of the curative substance does not appear to be borne out by his own experimental results.

[17] *This Journal, Sec. B* (1915), **10**, 99.

DIETHYLSUCCINOSUCCINATE: II

A STUDY OF THE ABSORPTION SPECTRA OF SOME DERIVATIVES[1]

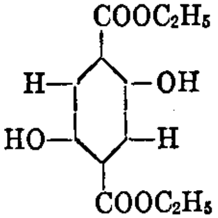
By HARVEY C. BRILL
(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

FOUR TEXT FIGURES

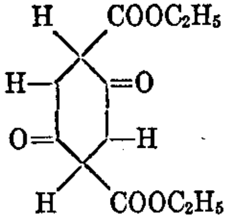
In a recent article by Gibbs and Brill[2] a study of the absorption spectra of diethylsuccinosuccinate and some derivatives was presented. It was shown that ethylsuccinosuccinate exists in the enol and keto forms with slightly different solubilities, thus allowing the separation of the one modification in partial freedom from the other; that the selective absorption of these compounds was due to the joint influence of the carbonyl and carboxyl groups; that the substitution of an acetyl group for the enol hydrogen destroys selective absorption in the case of succinosuccinate, but not in the case of salicylic acid; and the prediction was made that diketohexamethylene would show selective absorption.

In order to add evidence to these conclusions, some additional compounds have been prepared and examined under the iron-nickel arc.

p-DIOXYTEREPHTHALIC ESTER



or



This compound, which was mentioned by Geuther,[3] and proved to be the compound represented by the above formula by the investigation of Ebert,[4] was prepared by treating ethylsuccinosuccinate dissolved in carbon disulphide with bromine according to the method of Herrman.[5] The compound melted at 133°, the melting point given by the latter. It was titrated with alcoholic bromine solution[6] to determine the percentage content of enol and keto modifications. This titration showed that 90 per cent of *p*-dioxyterephthalic ester exists in alcoholic solution in the keto form and only 10 per cent in the enol form. The alcoholic solution was greenish yellow with a deep blue fluorescence under the arc. It showed two bands, one heading near the visible region at $1/\lambda=2,660$ and a much more refrangible one in the ultra-violet region at $1/\lambda=4,010$. This compound was also photographed in the presence of two equivalents of sodium ethylate. The same bands appear, and the position of the first lay largely in the visible region, heading at $1/\lambda=2,375$, while the second had not shifted.

---

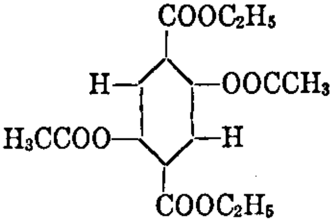
[1] Received for publication April 6, 1915.

[2] *This Journal, Sec. A* (1915), **10**, 51.

[3] *Ann. d. Chem.* (1883), **219**, 125.

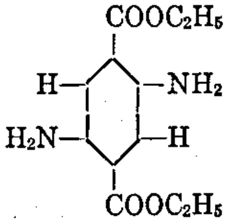
[4] Ibid. (1885), **229**, 45.

p-DIACETATE OF TEREPHTHALIC ESTER



The acetate was prepared in the manner described by Nef[7] for the preparation of the diacetyl derivative of succinosuccinate by treating the sodium salt of dioxyterephthalate with acetylchloride. After crystallizing from glacial acetic acid and later from alcohol, it was obtained in colorless white plates melting at 154°. The alcoholic solution gave only a very faint blue fluorescence in the light of the arc. An incipient band appears at $1/\lambda=2,900$, while a more decided band appears at $1/\lambda=3,390$.

p-DIAMIDOTEREPHTHALIC ESTER



---

[5] Ibid. (1882), 211, 327.
[6] Ibid. (1911), 380, 212.
[7] *Am. Chem. Journ.* (1890), 12, 416.

P-diamidoterephthalic ester was prepared by the method of Baeyer.[8] The compound dissolved in alcohol gave a reddish yellow solution which fluoresced bluish green in the light of the arc. The band appears in the visible region at $1/\lambda=2{,}310$, with a great increase in the general absorption in the ultra-violet region from $1/\lambda=3{,}500$ to $1/\lambda=4{,}200$. By adding an excess of hydrochloric acid, the solution became almost colorless, fluorescence was still visible in the light of the arc although less pronounced, and the band was shifted outside the visible region,

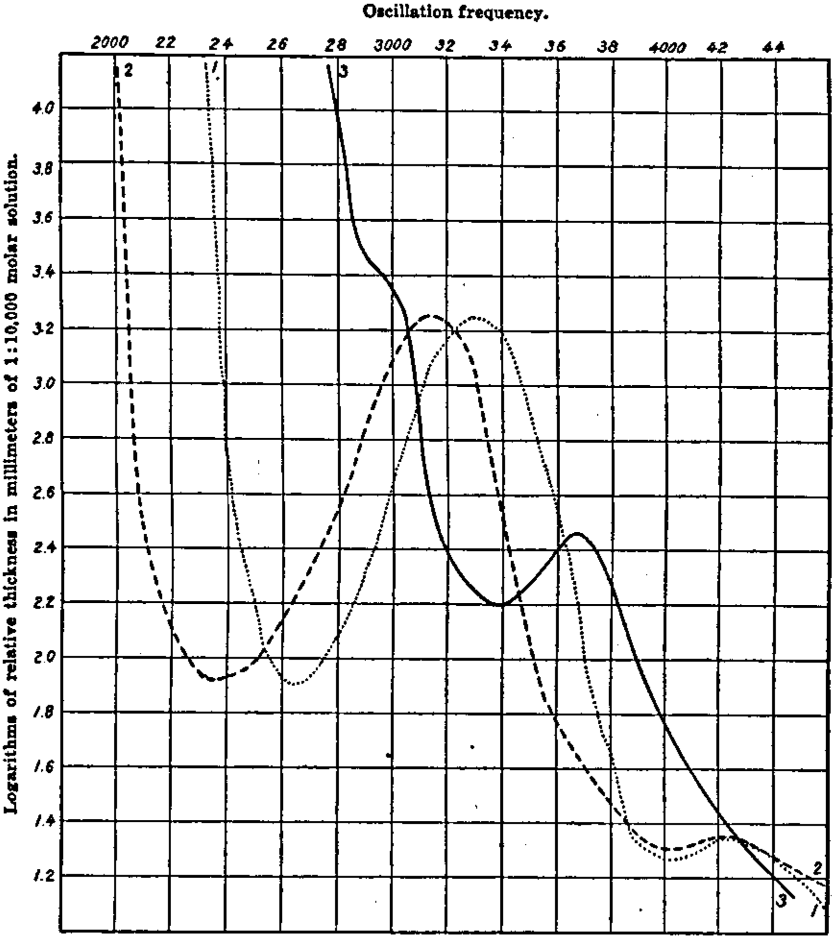


FIG. 1. *Curve 1.* Dioxydiethylterephthalate in alcohol. *Curve 2.* Dioxydiethylterephthalate in alcohol, plus 2 equivalents of sodium alcoholate. *Curve 3.* Diacetyl of dioxydiethylterephthalate in alcohol.

---

[8] *Ber. d. deutsch. chem. Ges.* (1886), 19, 430.

appearing at the same concentration as in the case of the free base.

Attempts were made to prepare the diimidodihydroterephthalate by treating p-dioxyterephthalate with ammonium acetate in the manner described for the preparation of the diimide of ethylsuccinosuccinate,[9] but without success.

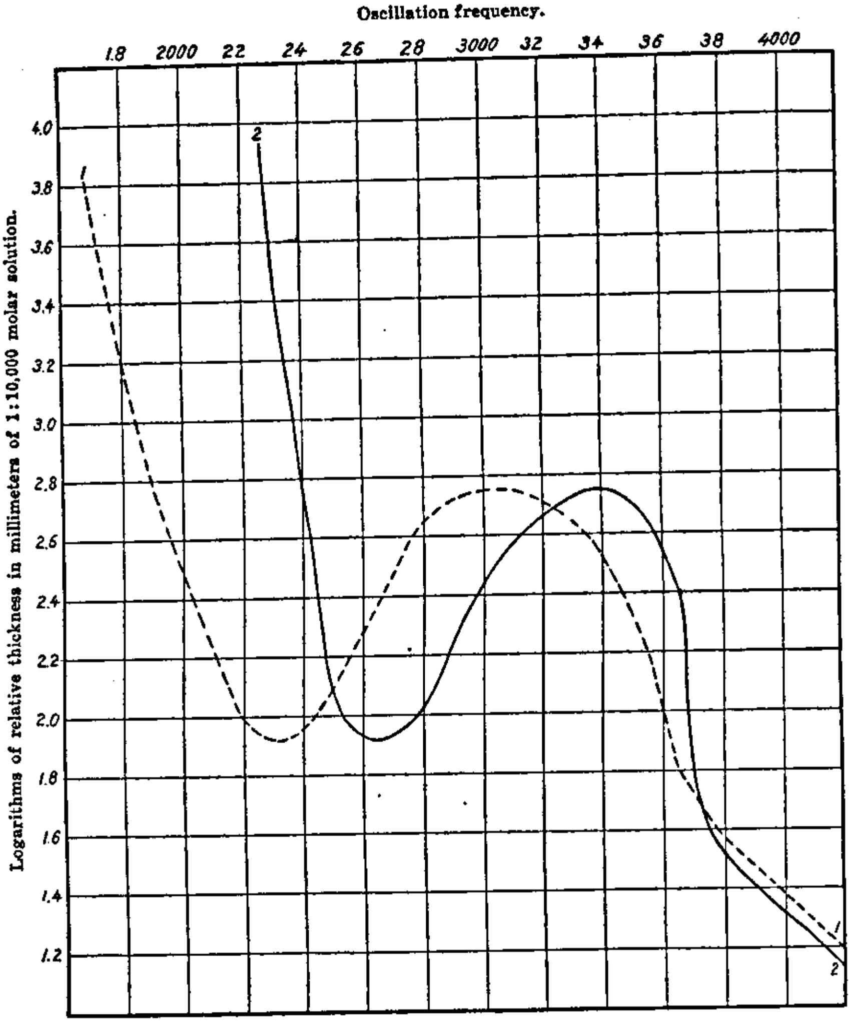
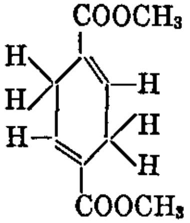


FIG. 2. *Curve 1.* Diamidodiethylterephthalate in alcohol. *Curve 2.* Diamidodiethylterephthalate in alcohol plus 2 equivalents of hydrochloric acid.

---

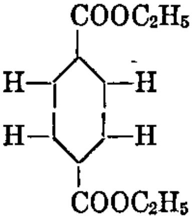
[9] Baeyer, ibid. (1886), 19, 430.

$\Delta_{1,4}$-DIHYDROTEREPHTHALIC ESTER



The $\Delta_{1,4}$-dihydroterephthalic methyl ester was prepared by treating a solution of the sodium salt of terephthalic acid with sodium amalgam[10] for some time, warming at intervals, and afterward forming the methyl ester by adding methyl alcohol to the intimate mixture of phosphorus pentachloride[11] and $\Delta_{1,4}$ dihydroterephthalic acid. This ester melts at 133° when purified by repeated crystallization from methyl alcohol, in which it is readily soluble. When photographed, a very shallow band is seen at $1/\lambda=3{,}480$ with a decidedly refrangible band at $1/\lambda=4{,}140$. The alcoholic solution shows slight blue fluorescence in the light of the arc.

TEREPHTHALIC ESTER



The ethyl ester of terephthalic acid prepared from terephthalic acid by the method used for the preparation of the methyl ester of dihydroterephthalic acid is a colorless crystalline body, melting at 43° C. when purified by crystallization from alcohol. It gives two rather well-defined bands in the ultra-violet region, one at $1/\lambda=3{,}480$ and the other at $1/\lambda=4{,}175$, at lower concentration than the bands for the dihydroterephthalate.

---

[10] Baeyer, *Ann. d. Chem.* (1889), 251, 290.

[11] Baeyer, ibid. (1888), 245, 140.

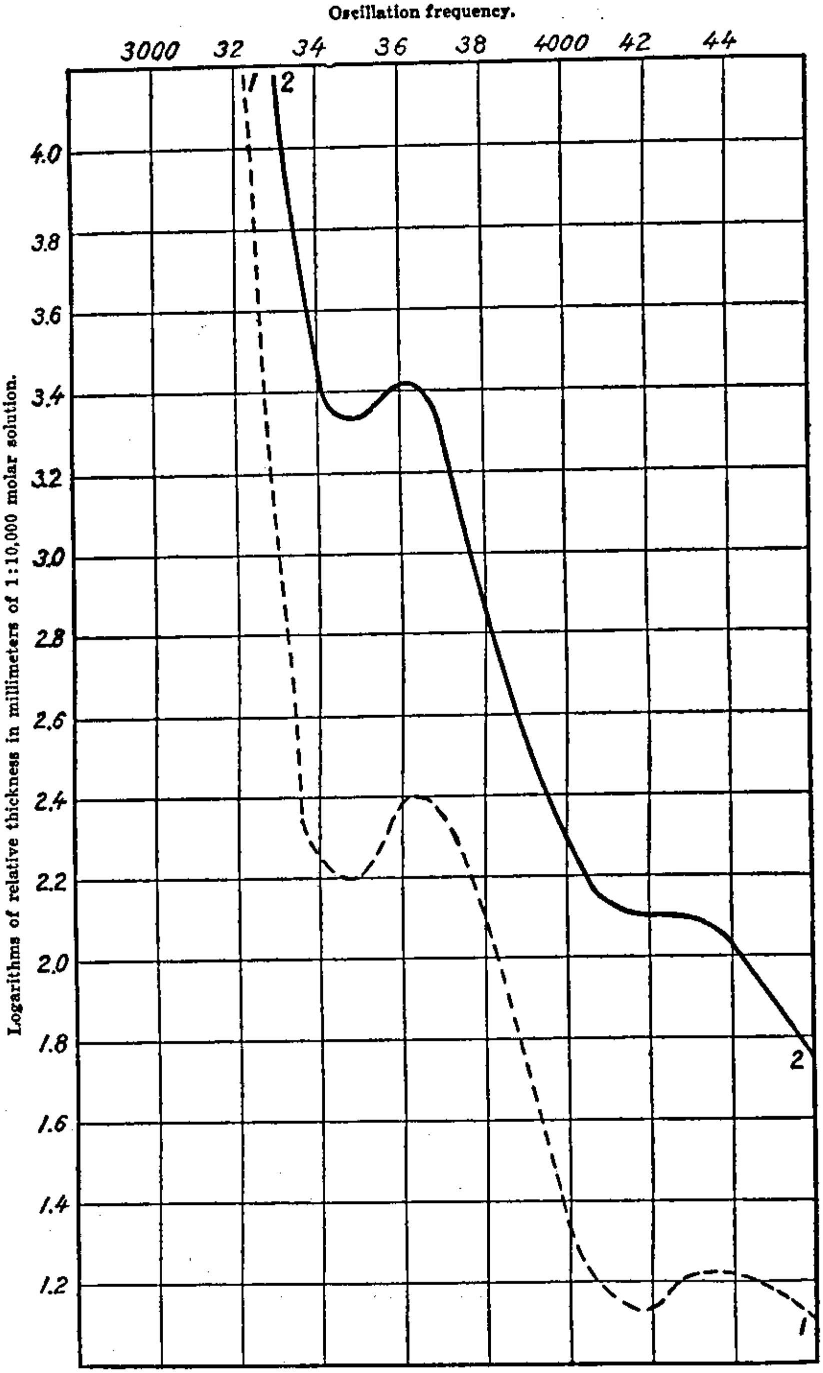
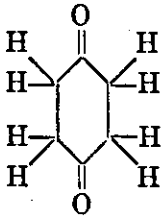


FIG. 3. *Curve 1.* Diethylterephthalate in alcohol. *Curve 2.* Diethyldihydroterephthalate in alcohol.

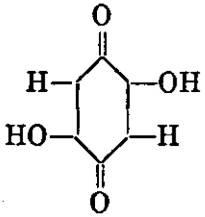
DIKETOHEXAMETHYLENE



Diketohexamethylene was made by the method described by Baeyer.[12] After repeated crystallizations it melted at 78°. It was examined immediately after having been crystallized, as it was noticed that on standing in a dessicator the compound slowly changed from pure white to a yellow tint. Titrated with bromine solution in accordance with the directions of Kurt H. Meyer,[13] it reacted for practically the pure keto form in alcohol solution.

In alcohol solution a very refrangible band appeared in approximately molar solution at $1/\lambda=3{,}500$.

p-HYDROXYQUINONE



Kehrman [14] describes a method for the preparation of hydroxyquinone by treating dianilinoquinone with a mixture of 3 parts of concentrated sulphuric acid and 2 parts of alcohol. However, as the yields obtained by me by the use of this method were exceedingly small, a modified method was adopted. Much better yields were obtained by warming dianilinoquinone in a tenth normal alcoholic potash solution on the steam bath under a reflux condenser until it had gone into solution and the solution had become a certain shade of red easily detected by experience. This usually required from three to five hours' warming. Alcohol of approximately 85 per cent strength was more influential to good yields than stronger alcohol. A large part of the alcohol was then distilled off in an open vessel on the steam bath, and the last portions allowed to evaporate in a vacuum dessicator or in the air at room temperature. Usually the heavy, dark red needles of the potassium salt crystallized out on standing. This crystallization could often be hastened by the addition of a few crystals of the salt. The free hydroxyquinone was then obtained from the salt by very carefully adding dilute sulphuric acid to the aqueous solution of the salt and extracting with ether.

---

[12] Ibid. (1894), 278, 91.

[13] Loc. cit.

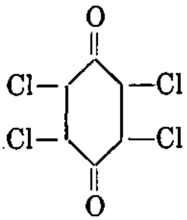
[14] *Ber. d. deutsch. chem. Ges.* (1890), 23, 903.

The quinone was obtained as a deep straw-yellow compound, decomposing without melting, very easily soluble in alcohol and alkalies, and readily turning brown on exposure to light.

The color of the alcoholic solution is due to general absorption in the red-color region, there being no color band, but a very rapid increase in general absorption from $1/\lambda=2,100$ to $1/\lambda=3,200$, with faint evidence of an incipient band heading at approximately $1/\lambda=2,400$. Selective absorption is shown by the compound in the ultra-violet region with a band at $1/\lambda=3,580$.

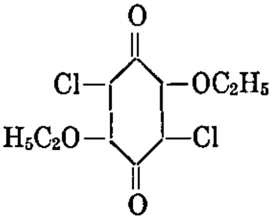
The potassium salt has caused a broadening of the incipient band of the quinone at $1/\lambda=2,400$ into a color band heading at $1/\lambda=2,030$. The second band is still present, although slightly shifted toward the red, heading now at $1/\lambda=3,450$.

CHLORANIL



Kahlbaum's chemically pure chloranil was recrystallized from glacial acetic acid and afterward photographed in this solvent. The olive-colored solution showed general absorption in the visible region, with a band appearing near, namely at $1/\lambda=2,725$, and a much deeper band in the ultra-violet region heading at $1/\lambda=3,520$.

p-DICHLORDIETHOXYQUINONE



Kehrman[15] prepared dichlordiethoxyquinone melting at 95–96° by treating an alcoholic suspension of chloranil at a temperature of 50° C. with a 1 per cent solution of alcoholic potash. Later[16] he claims to have prepared two modifications which he calls "allo-isomers," by treatment of chloranil with alcoholic potash at different temperatures.

His so-called α-compound melted at 107–108° C. Kehrman prepared this isomer by treating an alcoholic suspension of chloranil with alcoholic potash at a temperature near the boiling point of alcohol. It was obtained in the form of crystalline needles. The β-compound melting at 98° was formed by treating an ice-cooled alcoholic suspension of chloranil with a 1 per cent alcoholic potash solution. By this method he claims to have prepared the β-compound entirely free from the α-modification. In his preparation of the α-modification he freed it from the β-modification by making use of their difference in solubility in alcohol, the α-compound being more soluble in cold alcohol, but less soluble in hot than the β-compound. These compounds could not be transformed, the one into the other, by heating alone, with alkalies or with acids.

I have undertaken to make these two modifications in the manner described above, but without success in the case of the α-compound. Even with the most minute attention to the details of his method, no α-compound could be obtained, the β-compound resulting in every trial, and by repeated crystallization from alcohol no separation of this modification from the β-modification was attained.

The compound used here was prepared by treating an alcoholic suspension of chloranil with alcoholic potash at a temperature of 50° and later warming to boiling.[17] By repeated crystallization from alcohol, glacial acetic acid, and ether a platelike crystalline body was obtained melting at 96° C.

The alcoholic solution is chrome yellow, with a refrangible band in the color region heading at $1/\lambda=2,420$ and a second deeper band in the ultra-violet region heading at $1/\lambda=3,350$.

Attempts were made to prepare the oxime by treating a solution of the quinone with free hydroxylamine, but without success. Kehrmann[18] records unsuccessful experiments to prepare the oximes of tetra-substituted quinones by various methods and states that the oximes of such quinones cannot be obtained by direct treatment of the substituted quinone.

---

[15] *Journ. f. prakt. Chem.* (1889), 39, 318.

[16] Ibid. (1889), 40, 365.

[17] Kehrman, loc. cit.

[18] *Ber. d. deutsch. chem. Ges.* (1888), 21, 3315.

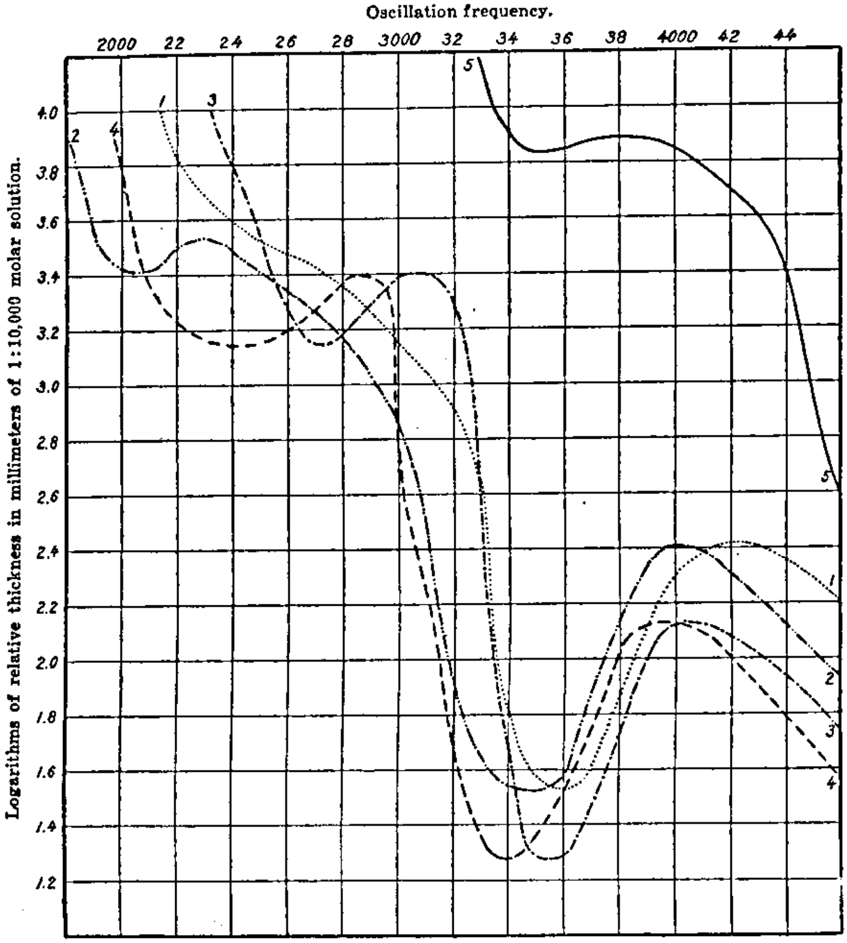


FIG. 4. *Curve 1. P*-hydroxyquinone in alcohol. *Curve 2.* Potassium salt of *p*-hydroxyquinone in 80 per cent alcohol. *Curve 3.* Chloranil in glacial acetic acid. *Curve 4. P*-dichlordiethoxyquinone in alcohol. *Curve 5.* Diketohexamethylene in alcohol.

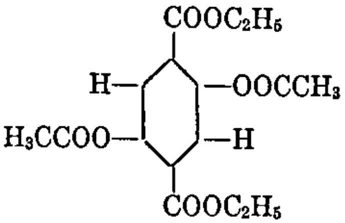
DISCUSSION OF RESULTS

Hydroxyterephthalic ester in the light of the arc shows an absorption curve differing somewhat in the intensity of its selective absorption from that of diethylsuccinosuccinate,[19] but heading at about the same point—namely, $1/\lambda=2,660$. In the former respect it more closely resembles salicylic acid,[20] the band of which heads at $1/\lambda=3,300$. The similarity of the bands of diethylsuccinosuccinate and of diethyldioxyterephthalate argues for a like cause of the absorption, and it was found that they were both made up of about 90 per cent enol form and 10 per cent keto form. The acetyl derivative of the latter still shows selective absorption, but the bands are shifted, heading at different points and appearing at different concentrations. The absorption curve is very similar to that found for acetyl methyl salicylate by Gibbs and Brill.[21] The constitution of these compounds is analogous; consequently one would expect to find the same type of absorption spectra and not have the selective absorption almost destroyed as is the case for the acetyl derivative of diethylsuccinosuccinate.

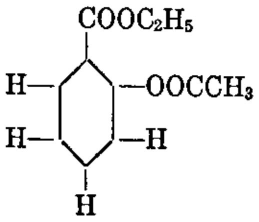
---

[19] Gibbs and Brill, loc. cit.

[20] Gibbs and Pratt, *This Journal, Sec. A* (1913), 8, 45.



Terephthalate.



Salicylate.

Diamidoterephthalic ester gives an absorption curve bearing a slight resemblance to that of the diimide of diethylsuccinosuccinate in that both head at $1/\lambda=2,300$, but the former appears at a lower concentration. When a slight excess of two molecules of hydrochloric acid is added, the band does not disappear, but is somewhat shifted toward the ultra-violet region, indicating that the free valencies of the nitrogen have not been saturated by the acid, but that the acid has been added to form a salt of the same character as that formed by thiophthaloxime[22] with sulphuric acid.

Baeyer[23] points out that dihydroterephthalic ester no longer possesses the properties of an aromatic compound, but must be classified as an aliphatic compound. However, it shows selective absorption, although to a less extent than terephthalic ester itself. If one accepts the partial valency theory as announced by Collie and adapted by Pratt[24] to be the explanation of selective absorption of light by organic compounds, a ready explanation of the occurrence of selective absorption of light in dihydroterephthalate is at hand. The double bonds of the ring are fixed by the addition of a molecule of hydrogen to the terephthalate; consequently no selective absorption of light waves can arise from the vibration of the bonds in the benzene ring, but must arise from oscillation of the double bonds of the carbonyl groups.

---

[21] Loc. cit.

[22] Pratt and Brill, *This Journal, Sec. A* (1914), 9, 115.

[23] *Ber. d. deutsch. chem. Ges.* (1886), 19, 1797; *Ann. d. Chem.* (1888), 245, 103.

[24] *This Journal, Sec. A* (1913), 8, 420.

Baly and Collie [25] state in regard to nitrobenzene—

> It seems probable that this very great absorption is due to some form of strained condition having been set up in the benzene molecule until the making and breaking of linking between the carbon atoms has ceased in nitrobenzene, and it seems not unlikely therefore that the presence of the active residual affinity as possessed by ketonic oxygen in the position tends to lock up or restrain the internal motions of the benzene ring.

The theory of partial valency as formulated by Pratt has the advantage of being simple enough to be understood readily, of portraying an easily grasped picture of the condition in the molecule, and of being broad enough to explain all the recorded instances of compounds possessing selective absorption, while the explanation of Baly and Collie, quoted above, presents a much more complex picture, which would be grasped only with exceeding difficulty and would not readily explain the occurrence of selective absorption in such compounds as dihydroterephthalic ester and diketohexamethylene. However, even they are agreed that the carbonyl oxygen has an important influence on the selective absorption of the compound.

To determine if the carbonyl groups alone possess the quality of selective absorption of light, diketohexamethylene, in which the bonds of the ring are all fixed, thus precluding their influence on the selective absorption, was photographed in the light of the iron-nickel arc. As predicted by Gibbs and Brill [26] in accordance with the theory of partial valency, this compound shows selective absorption giving a refrangible band heading at $1/\lambda=3{,}500$ and does not show only general absorption as noted by Hartley.[27]

Baeyer and Noyes [28] report that diketohexamethylene reacts with acetylchloride in ether solution, forming a white precipitate in the presence of sodium alcoholate and that, therefore, it may exist in two forms, the enol and keto. This acetyl compound was not stable and decomposed at once in the air. An attempt was made to photograph diketohexamethylene in the presence of two equivalents of sodium ethylate, but decomposition took place with darkening of the solution, and the absorption curve obtained was not different from the curve obtained from the solution of the compound alone. This result taken with that obtained by the titration of the alcoholic solution with alcoholic bromine solution is considered conclusive evidence that diketohexamethylene exists in alcoholic solution only in the keto form.

---

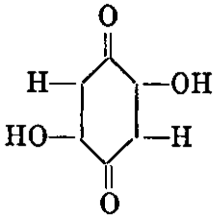
[25] *Journ. Chem. Soc.* (1905), 87, 1340.

[26] Loc. cit.

[27] *Journ. Chem. Soc.* (1898), 73, 598.

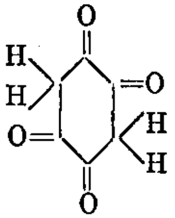
[28] *Ber. d. deutsch. chem. Ges.* (1889), 22, 2168.

Two forms are possible for *p*-hydroxyquinone.



Keto-enol.

and



Keto-keto.

As the potassium salt can exist in only the keto-enol form, chloranil in only the keto form, and dichlordiethoxyquinone in only the keto-enol form and as the absorption curves of these compounds are very similar, the evidence is fairly conclusive for the existence of *p*-hydroxyquinone in the keto-enol form.

SUMMARY

1. The absorption curves have been studied of dihydroxyterephthalate in alcohol, and in the presence of two molecules of sodium alcoholate; of *p*-diamidoterephthalate in alcohol, and in the presence of two molecules of hydrochloric acid; of diketohexamethylene in alcohol; of chloranil in glacial acetic acid; of *p*-hydroxyquinone in alcohol; of the potassium salt of the latter in dilute alcohol; and of dichlordiethoxyquinone in alcohol.

2. The spectra of both diketohexamethylene and dihydroterephthalate shows selective absorption, thus affording new evidence of the correctness of the theory that the selective absorption of organic compounds is intimately associated with the partial valency equilibrium of the compound.

ILLUSTRATIONS

TEXT FIGURES

FIG. 1. *Curve 1.* Dioxydiethylterephthalate in alcohol.
Curve 2. Dioxydiethylterephtalate in alcohol, plus 2 equivalents of sodium alcoholate.
Curve 3. Diacetyl of dioxydiethylterephthalate in alcohol.
2. *Curve 1.* Diamidodiethylterephthalate in alcohol.
Curve 2. Diamidodiethylterephthalate in alcohol plus 2 equivalents of hydrochloric acid.
3. *Curve 1.* Diethylterephthalate in alcohol.
Curve 2. Diethyldihydroterephthalate in alcohol.
4. *Curve 1.* *P*-hydroxyquinone in alcohol.
Curve 2. Potassium salt of *p*-hydroxyquinone in 80 per cent alcohol.
Curve 3. Chloranil in glacial acetic acid.
Curve 4. *P*-dichlordiethoxyquinone in alcohol.
Curve 5. Diketohexamethylene in alcohol.

HYDNOCARPUS VENENATA GAERTNER: FALSE CHAULMOOGRA[1]

By HARVEY C. BRILL

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Owing to the inaccessibility of the habitat considerable obscurity envelopes the source of the chaulmoogra oil of commerce which is used in the treatment of leprosy. For a long time it was supposed that this oil came from the seeds of *Gynocardia odorata* R. Br.,[2] and this belief has given rise to the name "oleum Gynocardiae," the name by which chaulmoogra oil is still often designated. However, true chaulmoogra oil is obtained from the seeds of *Taraktogenos kurzii* King,[3] although the oil from the seeds of *Hydnocarpus wightiana* Blume, *H. anthelminticus* Pierre, and *H. venenata* Gaertner, belonging to the same family, is probably often substituted for chaulmoogra oil. Oil from these last-named trees is known as "kavetel" in Malabar, also as false chaulmoogra oil in many places, and is so similar in all its properties that a distinction by chemical means is hardly possible.

Dr. E. E. Francis, chief medical officer, Asam-Bengal Railway, and technical adviser to the Indian Forests Economics Products Co. Ltd., in an open letter of February 21, 1914, to the editors of the pharmaceutical and medical journals in England, France, Germany, and America, quotes Mr. E. J. Parry as making the following statements in answer to questions put to him by certain vendors of these hydnocarpus oils:

> I would draw your attention, however, to the fact that persistent attempts have been made to restrict the description of chaulmoogra oil to the products of the seeds of Taraktogenos. Your oil is, in my opinion, the product of the seeds of Hydnocarpus which certain authorities consider the only genuine chaulmoogra oil.
>
> As a matter of fact the products from both seeds are so similar as to be nearly identical in properties, and I am of the opinion that your sample is properly described as chaulmoogra oil.
>
> I have examined the above described sample and am of the opinion that it is a genuine chaulmoogra oil free from any adulteration.

Doctor Francis attacks this opinion and challenges the good faith of Mr. Parry in making this statement and the vendors for selling hydnocarpus oils as a substitute for chaulmoogra oil.

---

[1] Received for publication November 6, 1915.

[2] Watt, Economic Products of India. W. H. Allen & Co., London (1890), **4**, 192.

[3] Brandis, Indian Trees. A. Constable & Co. Ltd., London (1907), 721.

The controversy aroused by the expressed opinion of Mr. Parry in regard to the oils included under the nomenclature chaulmoogra is illustrative of the uncertainty surrounding the sources and properties of these oils. Similar uncertainty is found in the literature elsewhere. The United States Dispensatory,[4] under *Gynocardia odorata,* gives the name of the oil as chaulmoogra oil and states that it owes its physiological activity to the presence of free gynocardic acid. This uncertainty should be cleared up as promptly as possible, since the well-being of a very unfortunate, large class of people is dependent on our accurate knowledge of the properties of chaulmoogra oil. Chaulmoogra oil is recognized as the most promising remedy for the treatment of leprosy. If the hydnocarpus oils have properties giving them similar physiological effects, to have this definitely proved will bring about a lowering in the cost of the chaulmoogra treatment, since larger quantities of oil will be available for use, and will allay the fear of fraudulent substitution of chaulmoogra by hydnocarpus.

Attention is called to the investigations directed by Mr. Power on the oils from the seeds of *Taraktogenos kurzii,*[5] *Hydnocarpus wightiana,*[6] *Hydnocarpus anthelminticus,*[7] and *Gynocardia odorata.*[8] It is the purpose of this article to present some data obtained by me in an investigation of the seeds of *Hydnocarpus venenata.*

A summary of the results obtained by investigators will be found in the latter part of this article.

HYDNOCARPUS VENENATA[9]

Hydnocarpus venenata belongs to the same family as *Taraktogenos kurzii, Hydnocarpus wightiana, Hydnocarpus anthelminticus, Hydnocarpus alcalae,* and *Pangium edule.* The last two species are indigenous to the Philippine Islands, and I hope to secure material for an investigation of their properties. There are other indigenous species of the Bixineæ which possibly may become sources of chaulmoogra oil.

---

[4] U. S. Dispensatory, 18th ed. (1899), 1678.

[5] Power and Gornall, *Journ. Chem. Soc. London* (1904), 85, 838.

[6] Power and Barrowcliff, ibid. (1905), 87, 884.

[7] Ibid. (1905), 87, 884.

[8] Ibid. (1905), 87, 896.

[9] These nuts were obtained through the kindness of Mr. H. G. Carter, economic botanist, Calcutta, India.

EXAMINATION OF THE SEEDS

Approximately 4 kilograms of the kernels, which had been heated at 100°C. for some time in order to destroy the activity of any enzymes present and afterward dried at a temperature between 80° and 90°C., were ground, and the oil was expressed. This oil is greenish yellow, possesses an odor resembling that of crude chaulmoogra oil, and is mobile at room temperature (30°C.).

The nuts yielded 45.57 per cent of dry kernels, which gave by expression a yield of 51.18 per cent of oil with the following properties:

The oil is optically active, being dextrorotatory.
Average rotation 30°/D for a 5-centimeter tube is +24.65°, making the specific rotation +52.03°.
Melting point, 19° to 20° C.
Specific gravity at 30°, 0.9475.
Index of refraction at 30° C., 1.4770.
Saponification value, 200.3.
Iodine value, 99.1.
Acid value cc. N/10 NaOH, 4.4.

EXAMINATION OF THE PRESS CAKE

The ground nuts and the press cake gave qualitative tests for hydrocyanic acid when crushed, suspended, and incubated at 38° C. for forty-eight hours in a solution of emulsin, indicating the presence of a cyanogenetic glucoside. Attempts were made to isolate this glucoside in the following manner: The press cake was extracted with strong alcohol, a large amount of glucose was removed from the alcoholic solution, the alcohol was recovered by distillation under a partial vacuum, and the resulting black, gummy residue was washed with ether to remove the fatty oil. The remainder was dissolved in water and extracted with chloroform. This resulted in a separation into two nearly equal portions. Both were concentrated to dryness, the chloroform portion in the air and the aqueous fraction in a vacuum dessicator over sulphuric acid. The dessicated aqueous extract was then extracted with hot absolute alcohol. This alcoholic solution was allowed to evaporate slowly in the hope that the glucoside would crystallize out, but without any success. In every trial, even after treatment with animal charcoal, infusorial earth, gypsum, etc., the resulting mass came out with a gummy consistency. This gum had the bitter taste of a cyanogenetic glucoside and gave qualitative tests for hydrocyanic acid and glucose. The product obtained by the treatment with alcohol was very small—about 1 gram from 4 kilograms of dry shelled nuts. On account of the small quantity of the material isolated, further attempts to obtain the glucoside in a pure state were discontinued. Nothing definite regarding the amount of the glucoside originally present can be adjudged from the small quantity of material isolated, since nothing is known concerning the previous history of the nuts received. They had the appearance of having been exposed to the weather; consequently hydrolysis of the glucoside due to the activity of the enzyme probably occurred. Fresh seeds have been requested in order that a quantitative determination of the amount of glucoside present can be made.

The water and chloroform portions were combined, acidified with hydrochloric acid, and subjected to steam distillation. The distillate gave tests for acetic and formic acids.

COMPOSITION OF THE OIL

One hundred grams of the oil were saponified with alcoholic potash, the alcohol was distilled off, and the dried mass was extracted with petroleum ether. An oil was extracted which on recrystallization from alcohol possessed a melting point of 132° C. and gave all the reactions of phytosterol.

For a complete examination of the fatty acids 500 grams of the oil were saponified with alcoholic potash and the acids were freed in the aqueous solution by the addition of acid. The free acids were then extracted with ether. A white solid mass was obtained with the following values: A melting point of 43° C., an iodine value of 102.9, a saponification value of 203.3, and specific rotation of +60.96°. The mixture of free acids was dissolved in alcohol with warming, and on cooling the part separating out was removed. After recrystallization from alcohol and ethylacetate it had a melting point of 68° C., identical with the melting point of the chaulmoogric acid found by Power and Barrowcliff[10] in the oil from *Taraktogenos kurzii*, *H. anthelminticus*, and *H. wightiana*. A solution of 2.071 grams in 50 cubic centimeters of chloroform produced in a 2-decimeter tube, a rotation of +4.95°, whence $[\alpha]^{30}_{D} = +59.75°$.

2.1409 grams required 76.16 cubic centimeters N/10 NaOH for neutralization. Theoretical, volume N/10 alkali for neutralization of 2.1408 grams $C_{17}H_{31}COOH$ requires 76.38 cubic centimeters.

0.7990 gram of the sodium salt gave 0.1862 gram Na_2SO_4, whence Na = 7.55 per cent. Theoretical for $C_{17}H_{31}COONa$ = 0.1878 gram Na_2SO_4, or Na = 7.62 per cent.

0.2029 gram absorbed 0.1833 gram iodine, whence I = 90.32 per cent. $C_{18}H_{32}O_2$ with one ethylenic linking requires I = 90.60 per cent.

---

[10] Loc. cit.

The alcoholic mother liquor from the chaulmoogric acid separation was then fractionally treated with a concentrated aqueous solution of barium acetate according to the method described by Power and others in the references cited. Five fractions of barium salts were obtained. The acid was freed by adding dilute sulphuric acid and extracting the resulting suspension with ether. The melting points of the fractions ranged: I, 48°; II, 53°; III, 43°; IV, 56°; V, 55°. Fractions IV and V on recrystallization from alcohol and ethylacetate melted at 59° to 60° C. This is the same melting point found by Power and Barrowcliff for hydnocarpic acid. Other values found for this acid are:

A solution of 1.7172 grams in 50 cubic centimeters of chloroform produced in a 2-decimeter tube a rotation of $+4.62°$, whence $[\infty]$ 30/D $= +67.26°$.

2.6095 grams required 102.2 cubic centimeters N/10 NaOH for neutralization. Theoretical for neutralization of 2.6095 grams of $C_{15}H_{27}COOH$ requires 103.4 cubic centimeters N/10 alkali.

1.0920 grams of the sodium salt gave 0.2808 gram Na_2SO_4, whence $Na = 8.33$ per cent. Theoretical for $C_{15}H_{27}COONa$ would give 0.2829 gram Na_2SO_4, or $Na = 8.38$ per cent.

0.1533 gram absorbed 0.1548 gram of iodine, whence $I = 101$ per cent. Theoretical for $C_{15}H_{27}COOH$ with one ethylenic linking requires $I = 100.6$ per cent.

DISCUSSION

The chemical constitution of the oils from *Taraktogenos kurzii, Hydnocarpus wightiana, Hydnocarpus anthelminticus*, and *Hydnocarpus venenata* is similar, but the oil from *Gynocardia odorata* is different. Table I gives the chemical properties of these oils.

TABLE I.—*Chemical constants of the oils from the seeds of Taraktogenos kurzii (chaulmoogric), Hydnocarpus wightiana, Hydnocarpus anthelminticus, Hydnocarpus venenata, and Gynocardia odorata.*

	Chaulmoogra.[a]	*H. wightiana.*[a]	*H. anthelminticus.*[a]	*H. venenata.*	*Gynocardia odorata.*[a]
M[illegible]g point	22°	22°	23°	20°	Liquid at 20°.
Specific gravity	0.951 at 25°	0.958 at 25°	0.953 at 25°	0.948 at 30°	0.925 at 25°.
Specific rotation	+52.0°	+57.7°	+25.5°	+52.03°	Inactive.
Iodine value	103.2	101.3	86.4	99.1	152.8.
Acid value	23.9	3.8	7.5	4.4	4.9.
Saponification value	213	207	212	200.3	197.
Index of refraction	1.476		1.473	1.477	
Cyanogenetic glucoside	Present	Present	Present	Present	Present.
Chaulmoogric acid	do	do	do	do	Absent.
Hydnocarpic acid	do	do	do	do	Do.

[a] Taken from the data published by Power et al. in the references already cited.

The oil from *Gynocardia odorata* can very easily be distinguished from the others because of its optical inactivity and the absence of chaulmoogric and hydnocarpic acids. A study of Table I will convince one that chemical tests will not give conclusive evidence in a differentiation of the other oils, since their constants are so similar. Reasoning from these properties one would expect the physiological action of the oils from the seeds of *Taraktogenos kurzii, Hydnocarpus wightiana, Hydnocarpus anthelminticus,* and *Hydnocarpus venenata* to be analogous, although perhaps varying in degree. If the physiological effects of these oils depend on the distinctive unsaturated acids present, the oil from *Gynocardia odorata* should act differently from the other four; on the other hand, if the activity is dependent on the presence of a cyanogenetic glucoside, the gynocardia oil should be as physiologically active as the others.

In a later paper I expect to be able to present some information as to the physiologically active portion of several of these oils.

SUMMARY

The results of an investigation of the chemical properties and constitution of the oil from the seeds of *Hydnocarpus venenata* are given.

These results would indicate that the physiological properties of the chaulmoogra and hydnocarpus oils should be identical, since the chemical constituents are identical, and that the properties of the gynocardia oil may be different, depending on whether the physiological activity is caused by the unsaturated acids present in the chaulmoogra and hydnocarpus oils or by the glucoside present in all the seeds.

THE SALICYLIC ACID REACTION OF BEANS[1]

By Harvey C. Brill

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

One of the most important economic plants with which man has to deal is the bean. It belongs to a group of plants called the pulse family, which contains members varying in size from the low annual plant to the tall broad-spreading tree. The bean is especially important since it not only furnishes food for man and beast, but enriches the soil in which it grows by taking nitrogen from the air and converting it into compounds available for plant growth. The Chinese and Japanese have recognized this fact from time immemorial, and their culture of the soy bean (*Glycine hispida*) has assumed large proportions. The shipments of dry beans from Manchuria are given in Table I.

TABLE I.—*Shipments of dry beans from Manchuria.*

	Tons.
1909	1,470,870
1910	1,200,000
1911	1,500,000

[a] Address, Soya bean oil as paint materials, by Maximillan Toch.

During the fiscal year 1914 there were imported into the Philippine Islands the quantities of beans recorded in Table II.

TABLE II.—*Dry beans imported into the Philippine Islands during 1914.*[a]

Country.	Quantity.		Value.	
	Kilos.	Per cent.	Pesos.[b]	Per cent.
China	1,763,015	63.00	131,272	41.70
Japan	501,022	17.90	64,146	20.40
Spain	113,409	4.05	30,560	9.70
United St[illegible]	415,805	14.85	86,904	27.65
All othe[illegible]	4,964	0.20	1,462	0.50
Total	2,798,215		314,344	

[a] Report, Philippine Bureau of Customs for 1914.

[b] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

China leads in the sales of beans in the Islands, followed by the United States and by Japan. Practically 60 per cent of

---

[1] Received for publication November 1, 1915.

the beans shipped into the Philippines—the combined shipments of China and Japan—are soy beans.

The consumption of beans by the inhabitants of the Archipelago is a good sign, indicating as it does the consumption of a more nearly balanced diet than can be obtained by the use of the common local cereals and vegetables, since the soy bean is a cheap source of protein matter and fat. It is superior to any other cultivated bean in this respect, as is proved by the data given in Tables III and IV.

TABLE III.—*Analyses of soy beans.*[a]

Variety.	Country.	Protein.	Fat.	Nitrogen free extract.	Protein and fat.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Soy black	Germany and France.	32.18	14.03	31.97	46.21
Soy yellow	China, Germany, and Austria.	33.41	17.68	29.31	51.09
Soy brown	do	32.90	18.03	30.17	50.93
Soy black, round	do	33.97	17.11	28.41	51.08
Unknown	France	35.00	13.60	29.92	48.60
Do	Japan	37.80	20.90	24.00	58.70
Do	India	36.00	18.00	25.00	54.00
Soy yellow	America	34.63	17.98	30.50	52.61
Soy white	do	27.56	19.09	28.24	46.64
Soy black	do	26.25	16.38	26.57	42.63

[a] Langworthy, *Farmers' Bull., U. S. Dept. Agr.* (1899), 58, 20.

TABLE IV.—*Analyses of kidney, frijole, and Lima beans, and of lentils, peas, and cowpeas.*[a]

Variety.	Protein.	Fat.	Carbohydrates.	Protein and fat.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Kidney beans	22.50	2.00	59.50	24.50
Frijoles	22.00	1.20	65.20	23.20
Lima beans	18.00	1.60	66.00	19.60
Lentils	26.00	1.00	[illegible]00	27.00
Peas	24.63	1.00	[illegible]	25.63
Cowpeas	21.40	1.40	[illegible]	22.80

[a] Abel, *Farmers' Bull., U. S. Dept. Agr.* (1900), 121, 20.

The maximum protein content, 37.80 per cent, for the soy bean is shown by a variety grown in Japan, while the maximum fat content, 20.90 per cent, is shown by the same variety; the minimum protein content, 26.25 per cent, is shown by a black variety grown in America, while the minimum fat content, 13.60

per cent, is shown by a black variety grown in Germany and France. Contrast these yields with the maximum protein content, 26.00 and 22.50 per cent, for lentils and kidney beans, respectively, and the maximum fat content, 1.40 and 2.00 per cent, for cowpeas and kidney beans, respectively, and the superiority of soy beans as an adjunct food for carbohydrates is very clearly brought out.

These beans are used in the preparation of so many and so varied kinds of foods, such as milk, cheese, casein, oil, jellies, flour, bread, biscuits, cakes, and sauces, that any information regarding their properties is particularly interesting and important; when these data are concerned with a property, such as the giving of a test for salicylic acid in the generally used ferric chloride color test, the recording of such data becomes doubly important. One very prominent duty of a government food laboratory is the testing of foods to determine if they are in accord with the laws regulating their preparation for consumption. The use of salicylic acid and the salicylates in foods has been prohibited.[2] In the light of this prohibition it seems very essential that the knowledge that a food under certain conditions gives this test should be generally known, in order that no injustice may be done to it.

In the test for salicylic acid, a substance volatile in steam, soluble in ether, capable of sublimation and crystallization, and giving a violet color with ferric chloride is usually considered to be salicylic acid.[3]

However, such a test is not conclusive evidence that salicylic acid is present.

Brand[4] found that an extract of caramel malt gave a reaction with ferric chloride like that given by salicylic acid. One year later he succeeded in isolating a crystalline substance ob-[illegible]ned by condensing the vapors given off during the roasting [illegible]-called m[illegible] coffee.[5] This compound is soluble in ether or [illegible]r (mu[illegible]ss soluble in cold water than in hot water), [illegible]ile i[illegible]n, a[illegible] a violet color with ferric chloride, b[illegible]es[illegible] giv[illegible] color with Millon's reagent which is [illegible]n by sali[illegible] acid. This compound, called maltol by Brand, he found to be phenolic in character and to agree with the formula $C_6H_6O_3$. The results obtained by Brand were corroborated by Erich[6] and Munsche.[7]

---

[2] *Food Inspection Decision, U. S. Dept. Agr.* (1907), 76.

[3] *Bull. U. S. Dept. Agr.* (1908), 107, 197; Leach, Food Inspection and Analysis. John Wiley & Sons, New York (1907), 671.

[4] *Zeitschr. f. d. ges. Brau.* (1893), 15, 303.

[5] *Ber. d. deutsch. chem. Ges.* (1894), 27, 806.

Kiliani and Bazlen[8] studied the chemical behavior of maltol. Will[9] studied its behavior toward yeast. Abraham[10] pointed out that dark-colored beers may readily contain maltol and that any test made for salicylic acid with ferric chloride which results positively could not be considered an absolute evidence of the presence of salicylic acid. He recommends the use of the Jorissen reaction.[11]

Jorissen's reaction.—To the solution to be tested add 4 to 5 drops of a 10 per cent solution of potassium nitrite, 4 or 5 drops of acetic acid, and 1 drop of a 10 per cent solution of copper sulphate and heat to boiling. In the presence of salicylic acid the solution turns reddish and in the presence of more than a trace it becomes blood red.

Jorissen points out that phenol reacts in the same manner with this reagent. However, phenol has no use as a preservative in foods, so offers few possibilities of confusion in this regard. Abraham recommends the reaction as the most reliable test for salicylic acid. He found that maltol gave no color with the Jorissen reagent.

Sherman[12] found a body similar to maltol in bread. He believes this body is formed during the process of baking. A. Backe[13] states that certain baked farinaceous foods, such as bread and biscuits, contain small quantities of a compound which show many of the reactions of salicylic acid. He believes the compound is produced when starchy foods and sugars are heated after being acted on by an unknown enzyme occurring together with ordinary amylase in flour and malt.

EXPERIMENTAL

The sentitiveness of ferric chloride solution, Millon's reagent, and Jorissen's reagent toward solutions of salicylic acid w[illegible] investigated. Ferric chloride gave a distinct violet color [illegible] a solution of 0.0008 gram salicylic acid in 100 cub[illegible]ntimete[illegible] water. This same solution gave a[illegible]ble [illegible] Joris[illegible] reaction. Millon's reagent reacted, giving a faint pink with a solution of 0.002 gram of salicylic acid in 100 cubic centimeters of water. I found it somewhat less sensitive than either the ferric chloride solution or the Jorissen reagent; consequently only the last two were used in the following tests.

---

[6] *Der Bierbrauer* (1893), 24, 465.

[7] *Wochenbl. f. Brauerei* (1893), 10, 739.

[8] *Ber. d. deutsch. chem. Ges.* (1894), 27, 3115.

[9] *Zeitschr. f. d. ges. Brau.* (1898), 21, 304.

[10] *Journ. Pharm. Liége* (1898), 5, 173.

[11] *Bull. Acad. Roy. Sci., Lettres, et Beaux Arts Belgique* (1882), III, 3, 259.

[12] *Journ. Ind. Eng. Chem.* (1910), 2, 24.

[13] *Compt. rend. Acad. Sci.* (1910), 150, 540.

Various methods of treatment were used in the preparation of the extract from the bean samples. The method described below gave the most satisfactory results: Fifty grams of the ground bean sample were allowed to stand for twenty-four hours, covered with 70 per cent alcohol. The use of 70 per cent alcohol prevented the extraction of large quantities of the fat. Extraction in a soxhlet with strong alcohol was tried, but it was found difficult to free the resulting extract from the fat, and the fat always interfered with the sensitiveness of the tests. They were then filtered with suction, the alcohol was carefully evaporated from the filtrate on the steam bath, the residue made slightly acid with dilute sulphuric acid and extracted with ether, the ether evaporated, and this residue dissolved in very dilute alcohol, made acid, and then tested with the testing reagents. The solution to be tested did not give a decidedly positive reaction except when acidified. Brand points out this difference in the properties of maltol and salicylic acid. This difference would serve as a means of differentiation, but is liable to error in the hands of a careless manipulator, since, if any of the acidified liquor is included in the ether extract, the conditions are present for a positive test for salicylic with ferric chloride solution.

Fifty grams of the ground beans which had given a positive test with iron chloride were suspended in water which was acidified with phosphoric acid and were then subjected to steam distillation.[14] The fractions passing over gave a positive test with iron chloride, but a negative test with Jorissen's reaction. [illegible] on several cereals and cereal products are included in [illegible] V.

TA[illegible] Res[illegible] on beans and several cereals.[a]

[illegible]	[illegible]ption.	Ferric chloride test.	Jorissen's reaction.
Philippine beans.			
1. Similar to Mexican	Brown beans	Positive	Negative.
2. Mongo	Yellow beans	Negative	Do.
3. Similar to navy	White beans	do	Do.

[a] Most of these examinations were made by F. W. Hauch, chemist, Bureau of Science.

---

[14] Sherman, *Journ. Ind. Eng. Chem.* (1910), 2, 24.

TABLE V.—*Results of tests on beans and several cereals*—Continued.

Origin and name.	Description.	Ferric chloride test.	Jorissen's reaction.
Japanese beans.			
1. Tokachi-mame	White with black spot; small.	Positive (about 0.02 per cent).	Negative.
2. Nakate-Ohsaya-Eda-mame.	White with black spot; large.	Positive (about 0.05 per cent).	Do.
3. Sodefuri-mame	Slightly green; large	do	Do.
4. Munada-Shiro-daidzu	do	do	Do.
5. Tanokuro-mame	Deep green with black spot; large.	Positive (about 0.025 per cent).	Do.
6. Shiro-mame	Yellow; large	Positive (about 0.075 to 0.1 per cent).	Do.
7. Tenruko-mame	do	Positive (about 0.05 to 0.1 per cent).	Do.
8. Snagoro-eda-mame	Yellow; small	do	Do.
9. Wase-Ohsaya-Eda-mame.	White; large	Positive (about 0.02 per cent).	Do.
10. Ao-daidzu	Deep green; large	Traces	Do.
11. Ao-Shiro-daidzu	Light green; large	Positive (about 0.008 to 0.01 per cent).	Do.
12. Gan-Wase-Eda-mame	Yellow with black spot; large.	Positive (about 0.03 to 0.05 per cent).	Do.
13. Kirro-mame	Black; large	Positive (about 0.05 to 0.075 per cent).	Do.
Chinese beans.			
1. American consul, Amoy, China.	Green; small	Positive (about 0.005 per cent).	Do.
2. American consul, Harbin district, down Sungari River.	Yellow with black spot; small.	Negative	Do.
3. District up Sungari River.	do	do	Do.
4. District along western line of Chinese Eastern Railroad.	do	Traces	Do.
5. District along eastern line of Chinese Eastern Railroad.	do	do	Do.
6. American consul, Amoy, China.	Black; small	Positive (about 0.05 to 0.075 per cent).	Do.
Chinese beans from American Consul, Mukden, Manchuria.			
1	White; small	[illegible]	Do.
2	Yellow; small	[illegible]	Do.
3	White; small	[illegible]	[illegible]
4	Red; small	Slight	[illegible]
5	Black; small	do	Do.
6	Green; small	Negative	Do.
American beans.			
1. Lima beans		do	Do.
2. Michigan navy		Traces	Do.
3. California navy		Negative	Do.
4. American peas		do	Do.

TABLE V.—*Results of tests on beans and several cereals*—Continued.

Origin and name.	Description.	Ferric chloride test.	Jorissen's reaction.
American beans—Cont.			
5. Cracked peas		Traces	Negative.
6. Kidney beans		Positive (about 0.025 to 0.05 per cent).	Do.
7. Mexican red beans		Negative	Do.
Breakfast foods.			
1. Grape nuts		Strongly positive	Do.
2. Quaker white oats		Negative	Do.
3. Quaker corn meal		do	Do.
4. Graham flour		do	Do.
5. Quaker wheat, puffed		do	Do.
6. Shredded wheat biscuit		do	Do.
7. Toasted corn flakes		do	Do.
8. Pop corn		do	Do.
Coffee substitutes.			
1. Lab. No. 120375	Roasted coffee and soy bean.	Strongly positive	Strongly positive.
2. Lab. No. 120384	do	do	Do.
3. Lab. No. 120388	do	Negative	Negative.
4. Lab. No. 120373	do	Strongly positive	Strongly positive.
5. Lab. No. 120381	do	do	Do.
6. Lab. No. 120378	do	Negative	Negative.
Flour.			
1. Lab. No. 120176		do	Do.
2. Lab. No. 120691		do	Do.
3. Lab. No. 120187-I		do	Do.
4. Lab. No. 120187-II		do	Do.
Tiqui-tiqui extract.			
1. Bureau of Science	Dilute alcoholic extract of rice polishings.	Slightest	Do.
2. Manuel Zamora	do	Negative	Do.
3. Botica de Santa Cruz	do	Slightest	Do.
Cacao.			
	Fermented	Negative	Do.
	Unfermented	do	Do.

[illegible]mbe[illegible] 7 [illegible]anese beans were cooked and then [illegible] same result as with the un-[illegible]nd 4 of the Japanese beans [illegible] suspended in [illegible] and allowed to stand for [illegible]gh hours until fermen[illegible] had actively begun and continued for some time. The s[illegible]sult was obtained as with the fresh beans—the amount o[illegible] reacting substance was not increased. Fermentation itself did not cause the formation of any of the reacting compound.

DISCUSSION

In the tests on the Japanese soy beans the ferric chloride test was positive in every case, usually strongly positive; the American, Chinese, and native beans tested gave either negative or somewhat faintly positive tests with ferric chloride. It would appear that the beans from Japan are slightly different from those of the other places cited. Climate, soil, or methods of handling could account for these differences in the tests given by the Japanese and Chinese beans, since the latter are soy. Fermentation alone did not bring about a synthesis of the reacting substance, as we have shown by experiment on Japanese soy beans, numbers 1, 2, 3, and 4. Brand has proved that malt which undergoes a peculiar kind of fermentation forms a compound giving the test. Sherman states that moisture and baking or roasting cause the formation of a similar compound in cereal products. He ignores in his statement the influence that the fermentation process which takes place before the baking of the bread on the addition of the yeast may have on the formation of this reacting substance. Among the breakfast cereals tested, grape nuts, which contains roasted wheat bread and malt, alone gave a positive test. Puffed wheat and shredded wheat biscuit which had been baked and had had moisture present when this baking process occurred gave negative results. This would indicate that moisture and baking are not sufficient to cause the synthesis of a reacting substance similar to maltol and would throw doubt on the surmise of Sherman that moisture and baking effects its formation. Backe, in his statements that the formation of the color substance is due to the action of an enzyme on farinaceous substances, seems much nearer the truth. As soy beans contain no starch, his statement would need to be broadened to include substances such as soy beans.

A very interesting test is the positive reaction given by [illegible] of the coffee-soy-bean mixtures with Jorisse[illegible] reagent [illegible] these are commercial products, we [illegible] w[illegible] accou[illegible] for the negative results in the [illegible] th[illegible] mise that the compound wa[illegible] roasting.

The reacting compound in [illegible] is volati[illegible] be sublimed, is soluble in di[illegible]ohol and in ether [illegible] a violet color with ferric [illegible]. In this respect it answers the requirements for the very generally used ferric chloride color test for salicylic acid, and it appears to be a compound similar in nature and composition to the maltol of Brand and the color compound found by Sherman to exist in baked farinaceous foods. By reason of the presence of a compound with the above enumerated properties, we believe Jorissen's reagent should be used in the test for the presence of salicylic acid in beans.

SUMMARY

The importance of the soy bean as an article of diet for the Philippine Islands has been shown.

These beans have been found to give the ferric chloride color test for salicylic acid and a negative test for salicylic acid with the Jorissen reagent and with the Millon reagent in the cases tried.

This compound is undoubtedly similar to the maltol of Brand, and I believe that it is formed by enzymic action in the beans.

MANI

PUBLICATIONS FOR SALE BY THE BUREAU OF SCIENCE, MANILA, PHILIPPINE ISLANDS—Continued

BOTANY

A FLORA OF MANILA

Elmer D. Merrill

Order No. 419. Paper, 490 pages, $2 postpaid.

Practically a complete flora of the [illegible]tivated areas in the Philippines. Descriptions, with keys, of over 1,000 species, 590 genera, and 136 families, with native names, glossary of technical terms, etc.

PHILIPPINE DIPTEROCARP FORESTS

By William H. Brown and Donald M. Mathews

Order No. 432. Paper, 150 pages, 1 map, 13 plates, and 12 diagrams, $1.00, postpaid.

In Philippine Dipterocarp Forests the authors present a very comprehensive discussion of the growth and development of dipterocarp trees and of the other elements of lowland Philippine forests.

INDO-MALAYAN WOODS

By Fred W. Foxworthy

Order No. 411. Paper, 182 pages, 9 plates, $0.50, postpaid.

In Indo-Malayan Woods, Doctor Foxworthy has brought together a large amount of accurate information concerning trees yielding woods of economic value.

ZOOLOGY

A LIST OF MAMMALS OF THE PHILIPPINE ISLANDS, EXCLUSIVE OF THE CETACEA

By Ned Hollister

Order No. 418. Paper, 64 pages, $0.50, postpaid.

The distribution of each species is given, and the original descriptions are cited.

ZOOLOGY—Continued

A MANUAL OF PHILIPPINE BIRDS

By Richard C. McGregor

Order No. 103. Paper, 2 parts, 769 pages, $4, postpaid.

A Manual of Philippine Birds contains in compact form descriptions of all the known species of Philippine birds. The usual keys and diagnoses of orders, families, and genera help the novice in identification.

A CHECK-LIST OF PHILIPPINE FISHES

By David Starr Jordan and Robert Earl Richardson

Order No. 102. Paper, 78 pages, $0.75, postpaid.

This list will be found a convenient guide to the synonymy of Philippine ichthyology. The nomenclature is thoroughly revised, and the distribution of each species within the Philippine Islands is given.

A CATALOGUE OF PHILIPPINE COLEOPTERA

By W. Schultze

Order No. 436. Paper, 198 pages, $1.00, postpaid.

This catalogue includes the names of all species of Coleoptera that have been recorded from a definite locality in the Philippine Islands. References to original descriptions and other important notes are given. The economic appendix includes comment on those species of beetles which are known to be injurious or beneficial to man.

PRICES ARE IN UNITED STATES CURRENCY

may be sent to the BUSINESS MANAGER,
E, BUREAU OF SCIENCE, MANILA, P. I.,
Please give order number.

e, New York, U. S. A.
London, W. C., England.
gue, Holland.
2, Berlin N. W., Germany.
ore, Straits Settlements.
bo, Ceylon.
India.

CONT NTS

Page.

WILLIAMS, ROBERT R. The chemis of the vitamines 49

BRILL, HARVEY C. Diethylsuccinosuccinate: II. A study of the absorption spectra of some derivatives 59

BRILL, HARVEY C. Hydnocarpus venenata Gaertner: False chaulmoogra 75

BRILL, HARVEY C. The salicylic acid reaction of beans 81

The "Philippine Journal of Science" is issued as follows:	U. S. currency.
Section A. Chemical and Geological Sciences and the Industries	$2.00
Section B. Tropical Medicine	3.00
Section C. Botany	2.00
Section D. General Biology, Ethnology, and Anthropology (Section D began with Volume V)	2.00
Entire Journal, Volume II, III, IV, or V	5.00
Entire Journal, beginning with Volume VI	7.00
Single numbers (except of Volume I)	.50
Each section is separately paged and indexed.	
Authors receive 100 copies of their papers free.	
Volume I, 1906 (not divided into sections) and supplement, sold only with a complete file of section A, B, or C	10.00
Supplement to Volume I (botany)	3.50
Volume I (without supplement), sold only with a complete file of section A, B, or C	6.50
Single numbers of Volume I	.75

Publications sent in exchange for the Philippine Journal of Science should be addressed: Library, Bureau of Science, Manila, P. I.

Subscriptions may be sent to the BUSINESS MANAGER, Philippine Journal of Science, Bureau of Science, Manila, P. I., or to any of the agents listed below:

AGENTS

The Macmillan Company, 64–66 Fifth Avenue, New York S. A.
Wm. Wesley & Son, 28 Essex Street, Strand W. land.
Martinus Nijhoff, Lange Voorhout 9, The
Mayer & Müller, Prinz Louis Ferdinands
Kelly & Walsh, Limited, 32 Raffles Pl
A. M. & J. Ferguson, 1
Thacker, Spink & Co., 1

64, Aven
Strand,
Entered 9, The H
ndstrass
Singa
Colom
lcutta